Novel Pentanuclear Iron(III) Complex with 2,6-Bis(salicylideneaminomethyl)-4-methylphenol

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A pentanuclear iron(III) complex with 2,6-bis(salicylideneaminomethyl)-4-methylphenol (H_3L), $[Fe_5(L)_2(O)(OH)_2(CH_3COO)_5(dmf)]\cdot C_6H_6\cdot 2H_2O$ (dmf = dimethylformamide) has been synthesized and characterized by magnetic susceptibilities (5—300 K). The X-ray crystal structure analysis has demonstrated that it consists of pentanuclear units where the Fe_5 framework has roughly a rectangular-based pyramidal geometry.

There is considerable current interest in the synthesis of multinuclear iron complexes, since these molecules might be useful as building blocks for "magnetic molecular materials"[1] and model compounds for understanding the properties of "ferritin", the iron storage protein of bacteria, plants, and animals.[2] A variety of multinuclear iron complexes containing dinuclear,[2] trinuclear,[2] tetranuclear,[2] hexanuclear,[2] octanuclear,[2] decanuclear,[3] undecanuclear,[2] dodecanuclear,[4] hexadecanuclear,[5] heptadecanuclear,[6] and nonadecanuclear[6] iron atoms have been reported so far. However, there has been no report on a pentanuclear iron complex. In order to achieve syntheses of multinuclear metal complexes, we are pursuing a method using dinucleating ligands.[7-9] In the course of this study, we have successfully isolated novel pentanuclear iron(III) complex by using 2,6-bis(salicylideneaminomethyl)-4-methylphenol (H_3L). Herein we report the synthesis and X-ray crystal structure of the pentanuclear iron(III) complex, $[Fe_5(L)_2(O)(OH)_2(CH_3COO)_5(dmf)]C_6H_6\cdot 2H_2O$ (dmf = dimethylformamide) (**1**).

The iron(III) complex **1** was synthesized as follows. Addition of a few drops of methanol solution of sodium hydroxide to a solution of H_3L (0.10 mmol) and basic iron(III) acetate (0.073 mmol) in a mixture of 4 ml of C_6H_6 and 0.5 ml of dimethylformamide resulted in the formation of **1**.[10] The structure revealed by X-ray crystallography[11] shows that a pentanuclear molecule is formed by association of the two dinuclear units by virtue of linking to the fifth iron moiety, $FeO(OH)_2(CH_3COO)_3$ (Figure 1). The five iron atoms in the cluster are arranged as a rectangular-based pyramid with Fe5 at the apex of the pyramid. The distances between the central metal atom (Fe5) and peripheral metal atoms (Fe1, Fe2, Fe3, and Fe4) vary from 3.370(4) [Fe1···Fe5] to 3.657(3) Å [Fe4···Fe5]. The distances between the peripheral metal atoms are in the range 2.960(4) [Fe1···Fe2]—5.367(4) Å [Fe2···Fe3]. The four peripheral Fe atoms form roughly a planar structure (±0.29 Å) and the central atom is 1.55 Å above this plane. In one dinuclear unit, the Fe1 and Fe2 atoms are bridged by a phenoxo-oxygen atom (O2) of the dinucleating ligand and one acetate ion. Similarly, in the other dinuclear unit, the Fe3 and Fe4 atoms are bridged by a phenoxo-oxygen atom (O5) of the dinucleating ligand and one acetate ion. These dinuclear units are connected to the Fe5 atom by oxo (O9), hydroxo (O7 and O8), and acetate ions forming the rectangular-based pyramidal Fe_5 framework. The Fe-O (oxo) distances [1.87(1)—1.92(1) Å] are significantly shorter than the Fe-O (hydroxo) distances [1.93(1)—2.01(1) Å]. This is consistent with the observed difference for multinuclear iron(III) complexes containing hydroxo and oxo bridges.[2,5] The coordination geometries of all the Fe atoms are distorted octahedra. The sixth coordination site of Fe4 is occupied by the oxygen atom of the dimethylformamide. This is the first example of a structurally characterized pentanuclear iron(III) complex containing dinucleating ligands.

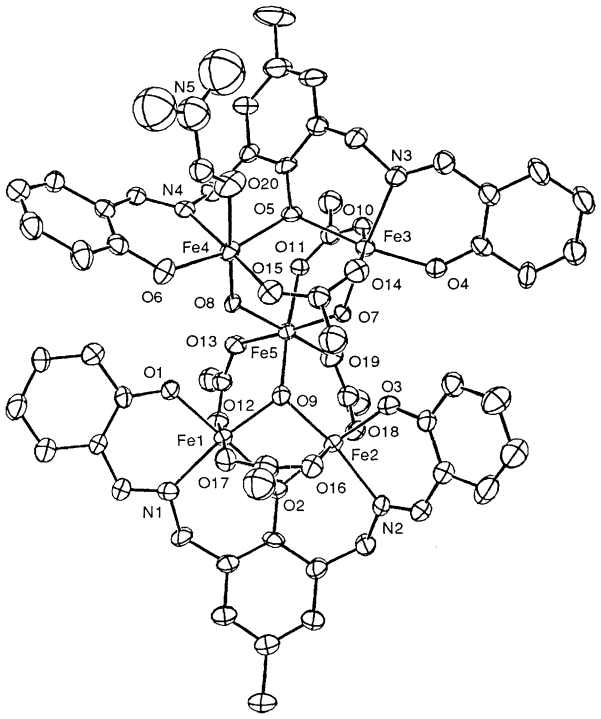

Figure 1. Structure of the pentanuclear iron molecule in **1**. Selected interatomic distances (Å) and angles (°): Fe1···Fe2 2.960(4), Fe1···Fe5 3.370(4), Fe2···Fe5 3.386(4), Fe3···Fe4 3.596(4), Fe3···Fe5 3.531(4), Fe4···Fe5 3.657(3), Fe1···Fe4 5.326(4), Fe2···Fe3 5.367(4), Fe1-O1 1.95(1), Fe1-O2 2.11(1), Fe1-O9 1.91(1), Fe1-O12 2.05(1), Fe1-O17 2.05(1), Fe1-N1 2.09(1), Fe2-O2 2.09(1), Fe2-O3 1.95(1), Fe2-O9 1.92(1), Fe2-O16 2.03(1), Fe2-O18 2.02(1), Fe2-N2 2.10(1), Fe3-O4 1.92(1), Fe3-O5 2.13(1), Fe3-O7 1.93(1), Fe3-O10 2.00(1), Fe3-O14 2.04(1), Fe3-N3 2.14(1), Fe4-O5 2.01(1), Fe4-O6 1.92(1), Fe4-O8 1.97(1), Fe4-O15 2.00(1), Fe4-O20 2.17(1), Fe4-N4 2.10(1), Fe5-O7 1.96(1), Fe5-O8 2.01(1), Fe5-O9 1.87(1), Fe5-O11 2.08(1), Fe5-O13 2.08(1), Fe5-O19 2.11(1); Fe1-O2-Fe2 89.7(5), Fe1-O9-Fe2 101.4(5), Fe1-O9-Fe5 126.4(6), Fe2-O9-Fe5 127.0(6), Fe3-O5-Fe4 120.6(5), Fe3-O7-Fe5 130.1(6), Fe4-O8-Fe5 133.5(6).

At 300 K the effective magnetic moment of **1** is 9.40 B.M. which is smaller than the expected one (13.23 B.M.) for five uncoupled S = 5/2 spins, but steadily increases on decreasing temperature, reaching a maximum of 16.37 B.M., at *ca.* 7 K. Below 7 K the magnetic moment decreases with decreasing temperature. The increase in effective magnetic moment with

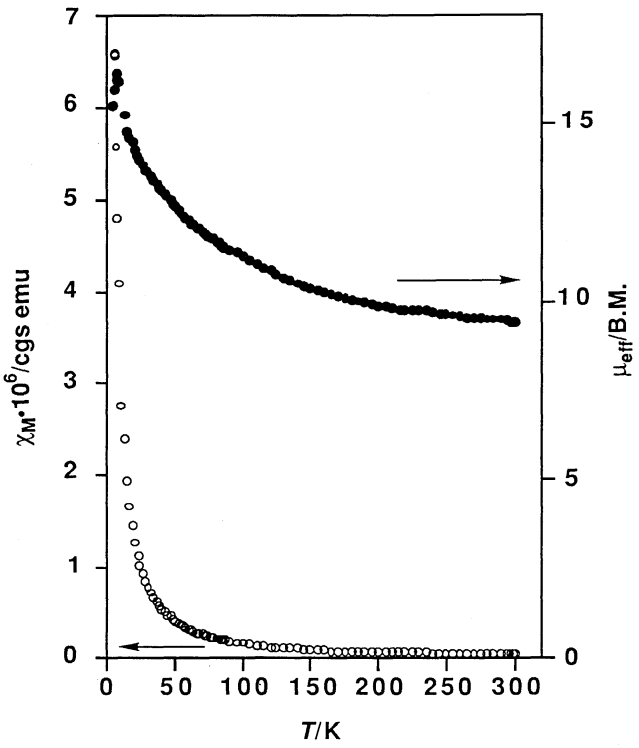

Figure 2. Temperature dependence of molar magnetic susceptibility and effective magnetic moment of **1**.

decreasing temperature indicates an increase in the average unpaired spin density at low temperatures relative to that found at room temperature. Although some multinuclear iron complexes with a high spin multiplicity in the ground state have been reported recently,[3] this type of behavior is still rare for a discrete multinuclear iron(III) complex. In this connection, it is noteworthy that the bridging angles Fe1-O2-Fe2 and Fe1-O9-Fe2 are unusually small. Such a small Fe-O-Fe angle has been found in the phenoxo-bridged dinuclear iron(III) complexes which show a ferromagnetic behavior.[12] In the present case, the exchange pathways involving the Fe1-O2-Fe2 and Fe1-O9-Fe2 bridges are probably responsible for the observed magnetism.

References and Notes

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10 Found: C, 49.78; H, 4.68; N, 4.73%. Anal. Calcd for $Fe_5O_{22}N_5C_{65}H_{72}$: C, 50.22; H, 4.67; N, 4.51%.

11 Crystal data for **1**: $Fe_5O_{22}N_5C_{65}H_{72}$, F.W.=1554.55, monoclinic, $P2_1/c$, a=16.498(6), b=20.514(6), c=22.529(9) Å, β=93.94(3)°, V=7606.5(47) Å^3, Z=4, D_m=1.39, D_c=1.36 g cm^{-3}, μ(Mo-Kα)=10.03 cm^{-1}. A total of 9730 reflections ($2\leq 2\theta\leq 46°$) were measured on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation; 5846 with $I\geq 3\sigma(I)$ were assumed observed. The structure was solved by the direct method and refined by the full-matrix least-squares method. The carbonyl carbon atom of the coordinated dmf molecule showed some disorder. This has been modelled and the occupancies refined to 60:40 for positions C57 and C57'. The refinement converged at R=0.092, R_w=0.131.

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